Certificate of Analysis

Standard Reference Material® 1632c

Trace Elements in Coal

(Bituminous)

This Standard Reference Material (SRM) is intended primarily for use in the evaluation of techniques employed in the analysis of coals and materials of a similar matrix. SRM 1632c consists of 50 g of bituminous coal ground to pass a 250 µm (60 mesh) sieve, homogenized, and bottled under an argon atmosphere.

Certified Values: The certified concentrations for 15 elements, expressed as mass fractions [1] on a dry basis, are provided in Table 1. The certified values for all elements, except sulfur, are based on two or more critically evaluated independent methods as described by Schiller and Eberhardt [2]. The certified value for sulfur is based on a single NIST primary method, isotope dilution thermal ionization mass spectrometry (ID-TIMS) [3]. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or accounted for by NIST [4].

Reference Values: The reference values for 25 constituents, expressed as mass fractions on a dry basis, are provided in Table 2. The reference values for carbon and nitrogen are based on two independent methods. The reference value for ash content is based on results from 64 laboratories participating in an interlaboratory study done in conjunction with the Canada Centre for Mineral and Energy Technology (CANMET) Service Program for the Evaluation of Codes and Standards (CANSPECS) using ASTM methods [5,6]. The reference values for other constituents are values from a single NIST analytical method. Reference values are noncertified values that are the best estimate of the true value; however, the values do not meet NIST criteria for certification and are provided with associated uncertainties that may reflect only measurement precision and may not include all sources of uncertainty [4].

Information Values: Information values for 13 selected elements, volatile matter content [6,7], and gross calorific value are provided in Table 3 for information purposes only. These are noncertified values with no uncertainty assessed. Summary statistics reported by CANSPECS for SRM 1632c, which was included as an unknown in the CANSPECS 54 Coal and CANSPECS 54 Ash Round Robins, are provided in the addendum to this certificate to demonstrate user experience with this material using conventional methods and to better characterize the matrix. The ash used in the CANSPECS 54 Ash Round Robin was prepared from the coal used to produce SRM 1632c and ashed in accordance with ASTM D 6357-00 [8]. The CANSPECS interlaboratory results should **NOT** be used as substitutes for NIST values.

Expiration of Certification: The certification of SRM 1632c is valid, within the measurement uncertainties specified, until **01 May 2010** provided the SRM is handled in accordance with the instructions given in this certificate (see Instructions for Use). This certification is nullified if the SRM is contaminated or otherwise modified.

Maintenance of SRM Certification: NIST will monitor representative samples of this SRM over the period of its certification. If substantive changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Return of the attached registration card will facilitate notification.

The technical and support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by B.S. MacDonald.

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Certificate Issue Date: 11 January 2001

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The coordination of the technical measurements leading to certification was performed by R.R. Greenberg of the NIST Analytical Chemistry Division.

Statistical analyses leading to certified and reference values were performed by J.H. Yen of the NIST Statistical Engineering Division.

The coal for this SRM was donated by Consol Coal Sales, Inc., Pittsburgh, PA.

INSTRUCTIONS FOR USE

Sampling: The SRM should be thoroughly mixed by rotating the bottle before sampling. A minimum sample mass of 250 mg should be used for analytical determinations to be related to elemental concentration values provided. The calorific value and ash content were determined using a minimum sample mass of 1 g. The SRM should be stored in its original, tightly sealed bottle away from sunlight and intense sources of radiation.

Drying: In order to relate measurements to the certified and reference values that are expressed on a dry mass basis, users should determine a drying correction at the time of each analysis. The correction is determined by oven drying a separate 1 g sample in a nitrogen atmosphere at 107 °C ± 3 °C to a constant mass [6]. During drying at NIST, the mass loss of SRM 1632c samples was observed to stabilize between 77 minutes and 91 minutes. The average mass loss measured at NIST for SRM 1632c was 2.02 % (1 s = 0.13 %, n = 12). Oven drying at 105 °C for 2 hours in an air atmosphere and desiccator drying for 5 days over fresh magnesium perchlorate are also acceptable drying methods. No significant difference between these two methods was observed. Moisture content determined by vacuum drying for 2 hours at ambient temperatures was found to be lower than oven or desiccator drying by about 0.5 % to 1 % absolute.

A NIST study was also conducted to quantify the difference between drying in air and nitrogen atmospheres for SRM 1632c. For the same time and temperature conditions, the average mass loss for oven drying the SRM in an air atmosphere was 1.97 % (1 s = 0.11 %, n = 12).

SOURCE, PREPARATION, AND ANALYSIS[1]

Source and Preparation of Material: The coal for this SRM was obtained from the Bailey Mine of the Consol Coal Company in southwestern Green County, PA. This mine produces bituminous coal obtained from the Pittsburgh seam which is considered to be one of the most extensively mined and economically important coal seams in the United States. The collection of the approximately 340 kg of washed coal was performed under the direction of L.W. Rosendale, Consol Coal Research and Development. The coal was air dried and subsequently pulverized to pass a 250 µm (60 mesh) sieve by a company under contract to NIST. At NIST, the entire lot was divided using the spinning riffle technique into two portions. One portion of the lot was sealed for long term storage in foil bags filled under an argon atmosphere. The remaining portion was further divided by the spinning riffler technique and bottled under an argon atmosphere. Several hundred bottles of the SRM 1632c lot were labeled SRM 1630a Trace Mercury in Coal and issued on 11 February 1999.

[1]Certain commercial equipment, instruments, or materials are identified in this certificate in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Table 1. Certified Mass Fractions for Selected Elements (Dry basis) in SRM 1632c

Major Constituents		Minor Constituents	
Elements	Mass Fraction (in %)	Elements	Mass Fraction (in %)
Hydrogen	5.11 ± 0.12	Potassium	0.1100 ± 0.0033
Sulfur	1.462 ± 0.051	Chlorine	0.1139 ± 0.0041

Trace Elements

Elements	Mass Fraction (in mg/kg)	Elements	Mass Fraction (in mg/kg)
Antimony	0.461 ± 0.029	Selenium	1.326 ± 0.071
Barium	41.1 ± 1.6	Sodium	298.8 ± 4.8
Cobalt	3.48 ± 0.20	Strontium	63.8 ± 1.4
Manganese	13.04 ± 0.53	Thorium	1.40 ± 0.03
Mercury	0.0938 ± 0.0037	Zinc	12.1 ± 1.3
Rubidium	7.52 ± 0.33		

The uncertainty in the certified value for sulfur is expressed as an expanded uncertainty, U, and is calculated according to the method described in the ISO Guide [9]. The observed sulfur variation was much greater than expected for the analytical technique used. Therefore, a prediction interval was used to account for the sulfur variability in this material. The expanded uncertainty is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined effect of uncertainty components associated with the measurement uncertainty and sulfur inhomogeneity, and k is a coverage factor. The coverage factor, $k = 2.3$, is determined from the Student's t-distribution with 8 degrees of freedom and corresponds to a 95 % prediction interval [10].

The uncertainties for all other certified values are weighted means of results from two or more analytical methods. For these certified values and reference values, the uncertainty is calculated as $U = ku_c + B$. The quantity u_c is the combined standard uncertainty calculated according to the ISO Guide [9], which accounts for the combined effect of the within variance for all methods at one standard deviation. The coverage factor, k, is determined from the Student's t-distribution corresponding to the appropriate associated degrees of freedom and 95 % confidence for each element. The term, B, is a bias adjustment for the difference between methods, which is the maximum difference between the certified value and the method means [2].

Table 2. Reference Values (Dry basis) for SRM 1632c

Major Constituents

Elements	Mass Fraction (in %)
Carbon (Total)	77.45 ± 0.25
Nitrogen	1.54 ± 0.06
Silicon	1.654 ± 0.034

Minor Constituents

Elements	Mass Fraction (in %)
Aluminum	0.915 ± 0.0137
Calcium	0.145 ± 0.030
Iron	0.735 ± 0.011
Magnesium	0.0384 ± 0.0032

Trace Elements

Elements	Mass Fraction (in mg/kg)	Elements	Mass Fraction (in mg/kg)
Arsenic	6.18 ± 0.27	Hafnium	0.585 ± 0.010
Boron	62 ± 2	Lead	3.79 ± 0.07
Bromine	18.7 ± 0.4	Nickel	9.32 ± 0.51
Cadmium	0.072 ± 0.007	Samarium	1.078 ± 0.028
Cerium	11.9 ± 0.2	Scandium	2.905 ± 0.036
Chromium	13.73 ± 0.20	Titanium	517 ± 32
Cesium	0.594 ± 0.010	Uranium	0.513 ± 0.012
Copper	6.01 ± 0.25	Vanadium	23.72 ± 0.51
Europium	0.1238 ± 0.0033		
Ash	7.16 ± 0.05		

The uncertainty in the carbon, nitrogen, and ash content reference values is calculated as an expanded uncertainty, $U = ku_c + B$. The quantity u_c is intended to represent, at the level of one standard deviation, the combined effect of within laboratory measurement uncertainty and between laboratory uncertainty [9]. The coverage factor, k, is determined from the Student's t-distribution with the appropriate associated degrees of freedom. The term, B, is a bias adjustment for the difference between methods, which is the maximum difference between the reference value and the method means [2].

The uncertainties for all other reference values are the expanded uncertainties calculated according to the ISO Guide [9].

Supplemental Information: The information values given in Table 3 are not certified and are given as additional information on the matrix. **NOTE:** Gross calorific value and volatile matter content [6,7] may decrease with time due to sample degradation.

Table 3. Information Values (Dry basis) for SRM 1632c

Elements	Mass Fraction (in mg/kg)	Elements	Mass Fraction (in mg/kg)
Beryllium	1.0	Silver	0.1
Bismuth	0.1	Tellurium	0.05
Gallium	3	Thallium	0.4
Germanium	5	Tin	1
Lithium	8	Yttrium	4
Molybdenum	0.8	Zirconium	16
Niobium	1		

Volatile Matter Content 36.0 %

Gross Calorific Value 32.10 $MJ \cdot kg^{-1}$ (13 802 $Btu_{th} \cdot lb^{-1}$)

Table 4. Methods of Analysis

Element	Method	Element	Method
Aluminum	INAA	Manganese	INAA, ICP-MS
Antimony	ICP-MS, INAA	Mercury	ID-CV-ICP-MS, RNAA
Arsenic	INAA	Molybdenum	ASTM D 6357
Ash	ASTM D 3174, ASTM D 5142	Nickel	ASTM D 6357, ICP-MS
Barium	INAA, ID-ICP-MS	Niobium	$\text{ICP-MS}^{\text{USGS}}$
Beryllium	ASTM D 6357, $\text{ICP-AES}^{\text{USGS}}$	Nitrogen	ASTM D 3179, INA
Bismuth	$\text{ICP-MS}^{\text{USGS}}$	Potassium	ID-ICP-MS, INAA, PGAA
Boron	PGAA	Rubidium	ID-ICP-MS, INAA
Bromine	INAA	Samarium	INAA
Cadmium	ICP-MS	Scandium	INAA
Calcium	INAA	Selenium	ICP-MS, INAA
Calorific Value	Commercial Coal Calorimeter	Silicon	WDXRF
Carbon (Total)	ASTM D 3178, ICA	Silver	$\text{ICP-MS}^{\text{USGS}}$
Cerium	INAA	Sodium	INAA, FES
Cesium	INAA	Strontium	ID-ICP-MS, INAA
Chlorine	ID-TIMS, PGAA, INAA	Sulfur	ID-TIMS
Chromium	INAA	Tellurium	$\text{ICP-MS}^{\text{USGS}}$
Cobalt	INAA, ICP-MS	Thallium	$\text{ICP-MS}^{\text{USGS}}$
Copper	ASTM D 6357, ICP-MS	Thorium	ID-ICP-MS, INAA
Europium	INAA	Tin	$\text{ICP-MS}^{\text{USGS}}$
Gallium	$\text{ICP-MS}^{\text{USGS}}$	Titanium	INAA
Germanium	$\text{ICP-MS}^{\text{USGS}}$	Uranium	ID-ICP-MS
Hafnium	INAA	Vanadium	INAA
Hydrogen	PGAA, ASTM D 3178, IHA	Volatile Matter	ASTM D 3175, ASTM D 5142
Iron	INAA	Yttrium	$\text{ICP-AES}^{\text{USGS}}$
Lead	ID-ICP-MS	Zinc	ICP-MS, INAA
Lithium	$\text{ICP-AES}^{\text{USGS}}$	Zirconium	$\text{ICP-AES}^{\text{USGS}}$
Magnesium	INAA		

Methods:

ASTM D 3178	Standard Test Methods for Carbon and Hydrogen in the Analysis Sample of Coal and Coke
ASTM D 3179	Standard Test Methods for Nitrogen in the Analysis Sample of Coal and Coke
ASTM D 6357	Standard Test Methods for Determination of Trace Elements in Coal, Coke, Combustion Residues from Coal Utilization Processes by Inductively Coupled Plasma Atomic Emission, Inductively Coupled Plasma Mass, and Graphite Furnace Atomic Absorption Spectrometries
FES	Flame emission spectrometry at NIST
FIA-CVAAS	Flow injection cold vapor atomic absorption spectrometry at NIST
$\text{ICP-AES}^{\text{USGS}}$	Inductively coupled plasma atomic emission spectrometry at United States Geological Survey (USGS)
$\text{ICP-MS}^{\text{USGS}}$	Inductively coupled plasma mass spectrometry at USGS
ICP-MS	Inductively coupled plasma mass spectrometry at NIST
ICA	Instrumental carbon analyzer
ID-CV-ICP-MS	Isotope dilution cold vapor inductively coupled plasma mass spectrometry at NIST
ID-ICP-MS	Isotope dilution inductively coupled plasma mass spectrometry at NIST
ID-TIMS	Isotope dilution thermal ionization mass spectrometry at NIST
IHA	Instrumental hydrogen analyzer
INA	Instrumental nitrogen analyzer
INAA	Instrumental neutron activation analysis at NIST
PGAA	Prompt gamma activation analysis at NIST
RNAA	Radiochemical neutron activation analysis at NIST
WDXRF	Wavelength dispersive X-ray fluorescence at NIST

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REFERENCES

[1] Taylor, B.N., "Guide for the Use of the International System of Units (SI)," NIST Special Publication 811, 1995 Ed., (1995).
[2] Schiller, S.B. and Eberhardt, K.R., "Combining Data from Independent Analysis Methods," Spectrochemical Acta, **46B** No. 12, pp. 1607-1613, (1991).
[3] Kelly, W.R., Paulsen, P.J., Murphy, K.E., Vocke, R.D., and Chen, L.-T. "Determination of Sulfur in Fossil Fuels by Isotope Dilution Thermal Ionization Mass Spectrometry," Anal. Chem., **66**, p. 2505, (1994).
[4] May, W.E., Gills, T.E., Parris, R., Beck, II, C.M., Fassett, J.D., Gettings, R.J., Greenberg, R.D., Guenther, F.R., Kramer, G., MacDonald, B.S., and Wise, S.A., "Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements," NIST Special Publication 260-136, (1999).
[5] ASTM D 3174-93, "Test Method for Ash in the Analysis Sample of Coal and Coke from Coal," ASTM Book of Standards **05.05**, West Conshohocken, PA.
[6] ASTM D 5142-90, "Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures," ASTM Book of Standards **05.05**, West Conshohocken, PA.
[7] ASTM D 3175-89a (1997), "Test Method for Volatile Matter in the Analysis Sample of Coal and Coke from Coal," ASTM Book of Standards **05.06**, West Conshohocken, PA.
[8] ASTM D 6357-00, "Standard Test Methods for Determination of Trace Elements in Coal, Coke, and Combustion Residues from Coal Utilization Processes by Inductively Coupled Plasma Atomic Emission Spectrometry, Inductively Coupled Plasma Mass Spectrometry, and Graphite Furnace Atomic Absorption Spectrometry," ASTM Book of Standards **05.06**, West Conshohocken, PA.
[9] *Guide to the Expression of Uncertainty in Measurement*, ISBN 92-67-10188-9, 1st Ed. ISO, Geneva, Switzerland, (1993); see also Taylor, B.N. and Kuyatt, C.E., "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results," NIST Technical Note 1297, U.S. Government Printing Office, Washington DC, (1994); available at http://physics.nist.gov/Pubs/.
[10] Hahn, G.J. and Meeker, W.Q., "Statistical Intervals: A Guide for Practitioners," John Wiley & Sons, Inc., NY, (1991).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet http://www.nist.gov/srm.

Addendum

Standard Reference Material® 1632c

Trace Elements in Coal (Bituminous)

CANSPECS 54 Coal Round Robin Results: SRM 1632c was included as an unknown in the February 1998 CANSPECS 54 Coal Round Robin. In addition, SRM 1632c coal was ashed in accordance to ASTM D 6357-00 [8] and included as an unknown ash in the February 1998 CANSPECS 54 Ash Round Robin. Summary statistics reported by CANSPECS are provided in the addendum to this certificate to demonstrate user experience with this material using conventional methods and to better characterize the matrix. The CANSPECS 54 Coal and Ash Round Robin results should **NOT** be used as substitutes for the NIST values.

Gaithersburg, MD 20899
Issue Date: 11 January 2001

Summary of Analysis Reported by CANSPECS

CANSPECS 54 Coal Sample NIST SRM 1632c

Parameter	Consensus Value	ASTM Method Referenced for Reproducibility and Repeatability	ASTM Reproducibility Standard Deviation	CANSPECS Reproducibility Standard Deviation	ASTM Repeatability Standard Deviation	CANSPECS Repeatability Standard Deviation	Number of Labs	Number of Methods
Moisture wt %	2.08	ASTM D 3173	0.11	0.13	0.07	0.06	79	22
Ash wt % db	7.16	ASTM D 3174	0.18	0.07	0.11	0.04	79	22
Volatiles wt % db	36.25	ASTM D 3175	0.35	0.87	0.18	0.19	65	17
BTU/lb db	13802	ASTM D 5865	44	64	18	18	73	16
Carbon wt % db	77.68	ASTM D 5373	0.89	0.78	0.23	0.22	33	14
Hydrogen wt % db	5.09	ASTM D 5373	0.11	0.20	0.06	0.07	32	13
Nitrogen wt % db	1.54	ASTM D 5373	0.06	0.07	0.04	0.03	34	13
Sulfur wt % db	1.49	ASTM D 4239c	0.05	0.05	0.03	0.02	77	18
Pyritic Sulfur wt % db	0.54	ASTM D 2492	0.10	0.12	0.05	0.02	16	4
Sulfate Sulfur wt % db	0.09	ASTM D 2492	0.01	0.05	0.01	0.01	16	3
Chlorine µg/g db	1127	ASTM D 4208	163	108	69	35	30	10
Fluorine µg/g db	70	ASTM D 3761	5	15	5	2	12	6
Mercury ng/g db	82	ASTM D 3684	11	13	7	8	15	8
Selenium µg/g db	1.32	ASTM D 4606	0.18	0.11	0.13	0.09	10	7
Free Swelling Index (FSI)	7.0	ASTM D 720	0.7	0.4	0.4	0.2	31	4

Summary of Analysis Reported by CANSPECS

CANSPECS 54 NIST SRM 1632c Laboratory Ash

Parameter	Consensus Value (in ash)	ASTM Method Referenced for Reproducibility and Repeatability	ASTM Reproducibility Standard Deviation	CANSPECS Reproducibility Standard Deviation	ASTM Repeatability Standard Deviation	CANSPECS Repeatability Standard Deviation	Number of Labs	Number of Methods
Al_2O_3 wt %	23.91	ASTM D 4326	1.03	0.74	0.29	0.24	34	11
Antimony mg/kg	6.0	ASTM D 6357	1.0	0.4	0.6	0.3	10	4
Arsenic mg/kg	78	ASTM D 6357	7	15	4	3	13	6
BaO wt %	0.060	ASTM D 4326	0.026	0.006	0.013	0.004	19	6
Beryllium mg/kg	13.5	ASTM D 6357	1.5	2.4	0.4	0.4	9	6
Cadmium mg/kg	1.1	ASTM D 6357	0.2	0.3	0.07	0.06	9	6
CaO wt %	2.76	ASTM D 4326	0.15	0.10	0.07	0.06	34	12
Chromium mg/kg	189	ASTM D 6357	13	22	6	3	16	9
Cobalt mg/kg	41	ASTM D 6357	3	8	2	0.7	11	7
Copper mg/kg	82	ASTM D 6357	8	7	3	3	14	8
Fe_2O_3 wt %	14.65	ASTM D 4326	0.53	0.50	0.10	0.17	34	11
K_2O wt %	1.75	ASTM D 4326	0.06	0.10	0.05	0.03	33	11
Lead mg/kg	46	ASTM D 6357	5	12	3	2	12	8
Manganese mg/kg	181	ASTM D 6357	13	12	7	3	15	8
MgO wt %	0.78	ASTM D 4326	0.07	0.03	0.04	0.02	32	11
Na_2O wt %	0.56	ASTM D 4326	0.15	0.06	0.07	0.02	33	12
Nickel mg/kg	126	ASTM D 6357	9	31	6	4	13	8
P_2O_5 wt %	0.466	ASTM D 4326	0.08	0.064	0.024	0.016	29	8
SiO_2 wt %	49.47	ASTM D 4326	1.56	1.31	0.45	0.28	33	11
SO_3 wt %	2.73	ASTM D 4326	0.47	0.28	0.16	0.03	31	12
SrO wt %	0.099	ASTM D 4326	0.050	0.008	0.014	0.003	17	7
TiO_2 wt %	1.09	ASTM D 4326	0.09	0.04	0.02	0.01	32	11
Vanadium mg/kg	324	ASTM D 6357	25	30	15	5	14	9
Zinc mg/kg	163	ASTM D 6357	11	31	6	4	14	9
Oxidizing Initial °C	1400	ASTM D 1857	20	9	11	4	20	1
Oxidizing Spherical °C	1435	ASTM D 1857	20	16	11	7	20	1
Oxidizing Hemi-spherical °C	1451	ASTM D 1857	20	11	11	6	20	1
Oxidizing Fluid °C	1471	ASTM D 1857	20	16	11	5	20	1
Reducing Initial °C	1193	ASTM D 1857	25	8	11	7	22	1
Reducing Spherical °C	1305	ASTM D 1857	20	43	11	6	22	1
Reducing Hemi-spherical °C	1338	ASTM D 1857	20	28	11	6	22	1
Reducing Fluid °C	1387	ASTM D 1857	30	27	11	7	22	1